

Structural Investigation on Layered α -Zirconium Phosphite and Zirconium Phosphate-Phosphites from X-Ray Powder Data

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During the last 20 years the α -layered salts of tetravalent metals with general formula $M(IV)(RXO_3)_2 \cdot nH_2O$, ($X = P, As; R = H, OH$, or organic radicals), have been intensively investigated and their crystalline structure (1, 2), ion exchange (2, 3), and intercalation properties (4) are now well known.

Recently a series of α -layered salts of zirconium with two different pendant groups, of general formula $Zr(RPO_3)_x(R'PO_3)_{2-x} \cdot nH_2O$ have been obtained (5-7). These compounds were found to exhibit ion-exchange and intercalation properties different from those of the corresponding $Zr(RPO_3)_2 \cdot nH_2O$ end members of the series.

Three different crystalline phases were observed (6) in the zirconium phosphate-phosphite system, $Zr(HPO_4)_x(HPO_3)_{2-x} \cdot nH_2O$, hereafter indicated as ZPP. The first one (ZPP-1), with x in the range 0-0.4, displays an X-ray pattern similar to that of pure $Zr(HPO_3)_2$. For the second one (ZPP-2), a structural model was initially as-

sumed, based on a regular distribution of phosphate and phosphite groups on both sides of each α -type sheet (6). Subsequently, this model appeared inadequate for explaining the ion-exchange and intercalation behavior of this material. The third phase (ZPP-3), with $x = 1.4-2.0$, is characterized by an X-ray pattern similar to that of $Zr(HPO_4)_2 \cdot H_2O$.

A research program has been undertaken to elucidate the structural features of mixed α -layered compounds, starting from the above zirconium phosphate-phosphites. It is the aim of this paper to report briefly the main results concerning the latter compounds.

Experimental

Samples of ZPP were prepared by a very fast precipitation in the presence of HF (8). The refluxing method (9) with short refluxing times was followed in the synthesis of $Zr(HPO_3)_2$ and $Zr(HPO_4)_2 \cdot H_2O$. The smallest particles, separated by sedimentation procedure, were used for X-ray analysis, in

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order to minimize possible preferred orientation. X-Ray data were collected on side-loaded samples throughout the 5–80° 2 θ angular region; the step scanning procedure was applied with a step size of 0.03°. A computer-controlled Philips powder diffractometer with CuK α radiation was used. Indexing of the patterns was attempted by considering the structure of α -Zr(HPO₄)₂ · H₂O (10) as a reference point. The unit cell parameters were obtained from a least-squares fit of the interplanar spacing of 10–15 selected reflections.

Calculation of the X-ray profiles was performed in steps of 0.03° 2 θ by means of a computer program written in our Laboratories. A Lorentzian peak-profile function was assumed, according to a theoretical background (11) relating the half-peak width to the average crystal size along the three edges of the unit cell, L_a , L_b , and L_c , respectively. Two separate peaks were calculated for each reflection, corresponding to $K\alpha_1$ and $K\alpha_2$ wavelength, respectively, with integrated intensity in the 2:1 ratio. The instrumental broadening was taken into account according to a procedure already applied by us in a similar investigation and described in a recent paper (12). Atomic scattering factors were from Cromer and Mann (13) for non-hydrogen atoms

and from Stewart *et al.* (14) for hydrogen. No least-squares structural refinement was performed at this stage of the work, the values of L_a , L_b , and L_c having been varied by trial and error method to fit the experimental peak-profile.

Results and Discussion

Pure α -Zr(HPO₃)₂ was included in the structural investigation of ZPP, its crystal structure being unknown. The powder pattern of this compound is clearly interpreted on the basis of a trigonal unit cell (Table I). A structural model was devised for which Zr atom is located on $\bar{3}$ while P and H atoms are located on 3-symmetry element, according to the assumed $P\bar{3}$ space group. The oxygen atom was placed in such a way to obtain a regular octahedral coordination of zirconium with a Zr–O and P–O bond distances of 2.064 and 1.517 Å, respectively (corresponding to the average values observed in Zr(HPO₄)₂ · H₂O (10)).

A P–H bond distance of 1.43 Å was assumed. The resulting H–P–O bond angle is 108°. This model, characterized by the fractional coordinates reported in Table II, gives a very good profile fitting of the experimental pattern (Fig. 1). The resulting

TABLE I
CRYSTAL DATA

| | Unit cell parameters | | | | Crystal symmetry | Space group |
|--|----------------------|---------|---------|-------------|------------------|--------------------|
| | a (Å) | b (Å) | c (Å) | β (°) | | |
| Zr(HPO ₃) ₂ ^a | 5.418 | | 5.579 | | Trigonal | $P\bar{3}$ |
| Zr(HPO ₄) _{0.36} (HPO ₃) _{1.64} ^b | 5.41 | | 11.60 | | Trigonal | $P\bar{3}$ |
| Zr(HPO ₄) _{0.85} (HPO ₃) _{1.15} 0.5H ₂ O ^b | 9.33 | 5.39 | 14.35 | 115.7 | Monoclinic | C2 |
| Zr(HPO ₄) _{1.46} (HPO ₃) _{0.54} H ₂ O ^b | 9.11 | 5.33 | 15.28 | 101.8 | Monoclinic | P2 ₁ /n |
| Zr(HPO ₄) ₂ H ₂ O ^a | 9.06 | 5.29 | 15.46 | 101.7 | Monoclinic | P2 ₁ /n |
| Zr(HPO ₄) ₂ · H ₂ O ^c | 9.060 | 5.297 | 15.414 | 101.71 | Monoclinic | P2 ₁ /n |

^a Prepared by refluxing method.

^b Prepared by HF procedure.

^c Single crystal. Data from Ref. (10).

TABLE II
POSITIONAL AND THERMAL PARAMETERS USED IN
THE CALCULATION OF X-RAY PROFILES FOR
 $Zr(HPO_3)_2$ AND $Zr(HPO_4)_{0.85}(HPO_3)_{1.15} \cdot 0.5H_2O$

| (1) $Zr(HPO_3)_2$ | | | | |
|---|---------------|---------------|---------------|-----|
| | X | Y | Z | B |
| Zr | 0 | 0 | 0 | 0.5 |
| P | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.298 | 0.7 |
| O | 0.180 | 0.820 | 0.214 | 1.5 |
| H | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.554 | 2.0 |
| $L_a = 1000 \text{ \AA}^a$; $L_b = 1000 \text{ \AA}^a$; $L_c = 500 \text{ \AA}^a$ | | | | |
| (2) $Zr(HPO_4)_{0.85}(HPO_3)_{1.15} \cdot 0.5H_2O$ | | | | |
| | X | Y | Z | B |
| Zr | 0.144 | 0.750 | 0.216 | 0.5 |
| P1 | 0.065 | 0.250 | 0.348 | 0.7 |
| P2 | -0.278 | 0.750 | 0.083 | 0.7 |
| O1 | -0.114 | 0.250 | 0.308 | 1.5 |
| O2 | -0.098 | 0.750 | 0.124 | 1.5 |
| O3 | 0.115 | 0.021 | 0.308 | 1.5 |
| O4 | -0.327 | 0.979 | 0.124 | 1.5 |
| O5 | 0.115 | 0.479 | 0.308 | 1.5 |
| O6 | -0.327 | 0.521 | 0.124 | 1.5 |
| O7 ^b | 0.146 | 0.250 | 0.469 | 2.0 |
| OW ^c | 0 | 0.750 | $\frac{1}{2}$ | 3.0 |
| H1 ^d | 0.139 | 0.250 | 0.459 | 3.0 |
| H2 | -0.352 | 0.750 | -0.027 | 3.0 |
| $L_a = 1000 \text{ \AA}^a$; $L_b = 1000 \text{ \AA}^a$; $L_c = 150 \text{ \AA}^a$ | | | | |

^a Average crystal size along *a*, *b*, and *c* axis, respectively, see text.

^b OH of HPO_4 groups, occupancy factor of 0.85.

^c Oxygen of water molecule.

^d Hydrogen of HPO_3 groups in the phosphate type region, occupancy factor of 0.15.

structure of the sheet of $Zr(HPO_3)_2$ is very similar to that of the sheet of the well-known α - $Zr(HPO_4)_2 \cdot H_2O$ (*I*, *I0*) which deviates slightly from the ideal trigonal symmetry. The schematic model of α - $Zr(HPO_3)_2$ is shown in Fig. 2a. Note that α - Zr phosphite and α - Zr phosphate exhibit two different types of stacking of the characteristic α -type sheet; the first corresponds to a simple translation perpendicular to the sheet plane, the interlayer distance being 5.53 Å. The second is obtained by a glide

plane symmetry operation, the interlayer distance being 7.56 Å.

A structural model was postulated for ZPP-2, as schematically shown in Fig. 2c, according to the monoclinic unit cell which fits the experimental X-ray pattern (see Table I). The distribution of phosphates and phosphite groups within each sheet is not homogeneous, one side being richer in phosphate, the other containing only phosphite groups (some phosphate groups may be present as occasional impurity). These asymmetric sheets are arranged in such a way that a regular alternation of phosphate and phosphite type of stacking occurs. This results in a regular alternation of an interlayer region of the α -zirconium phosphate type with an interlayer region of the α -zirconium phosphite type. Water molecules are placed in the phosphate-type interlayer region, as in the pure zirconium phosphate. A model was considered, with the same sheet structure of $Zr(HPO_3)_2$ and a random distribution of OH and H groups within the phosphate-type region. A P-OH bond distance of 1.56 Å was assumed, as observed in α - $Zr(HPO_4) \cdot H_2O$ (*I0*). The C_2 space group was assumed according to the systematic absences of *hkl* with $h + k = 2n + 1$ and in line with the expected symmetry of the lattice. The fractional coordinates of the independent structural unit are reported in Table II, corresponding to $x = 0.85$. A calculated profile is obtained with this model, which is in satisfactory agreement with the experimental pattern (see Fig. 3). The main discrepancies seem to arise from some preferred orientation present in the experimental pattern, as indicated by the opposite trend displayed by lattice planes parallel [(002), $2\theta = 13.7^\circ$] and perpendicular [$(\bar{2}01)$, (111), $2\theta = 19.1^\circ$ and (312), (020), $2\theta = 33.2^\circ$], respectively.

Models based on a symmetric sheet structure (one type of interlayer distance only) are clearly inconsistent with the presence of (001) reflection ($2\theta = 6.8^\circ$).

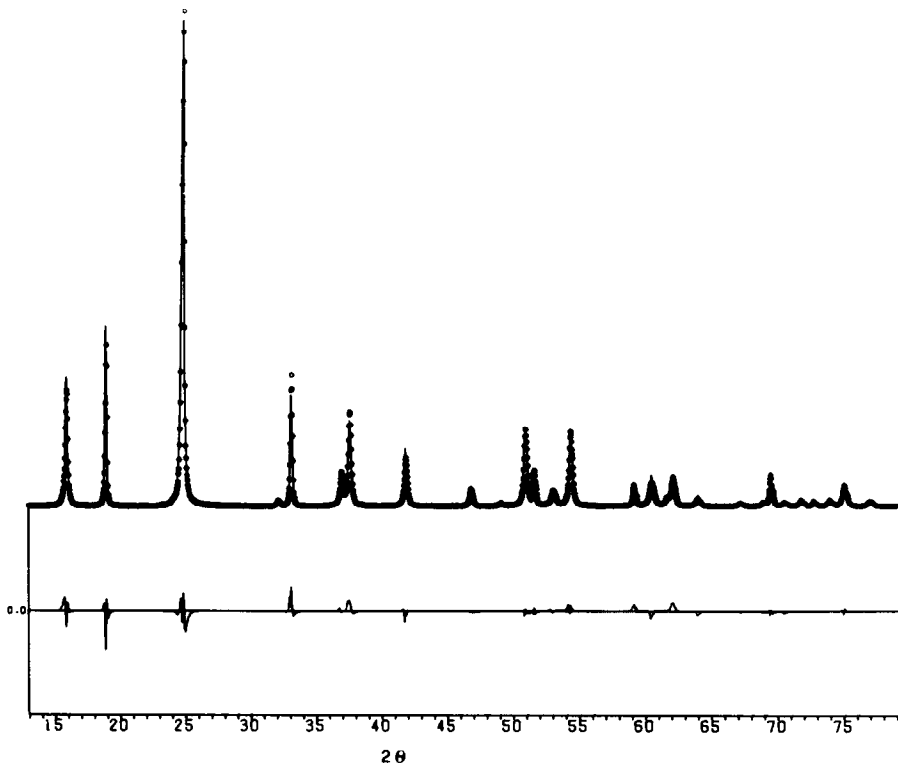


FIG. 1. Experimental (○), calculated (—), and difference (lower) profiles for $\text{Zr}(\text{HPO}_3)_2$.

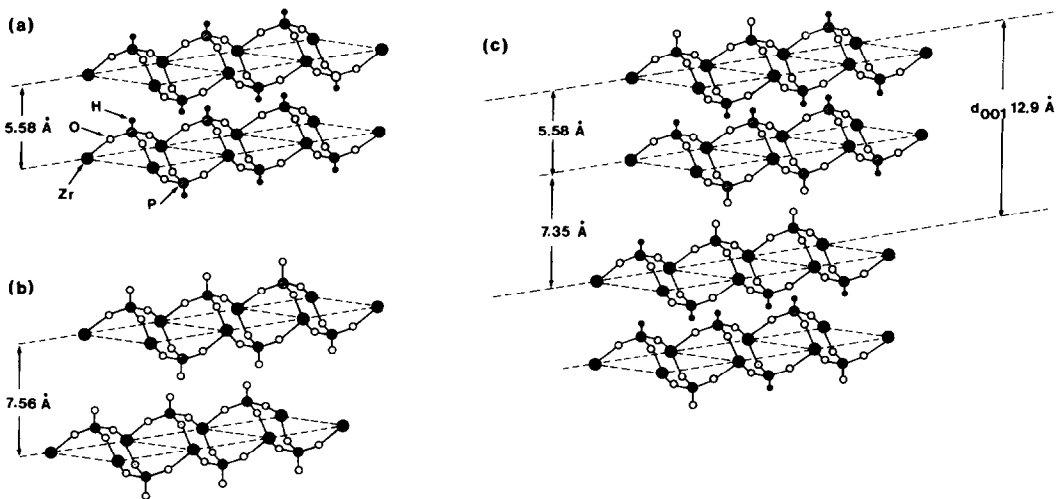


FIG. 2. Schematic model of the structure of (a) zirconium phosphite, (b) zirconium phosphate, (c) zirconium phosphate-phosphite.

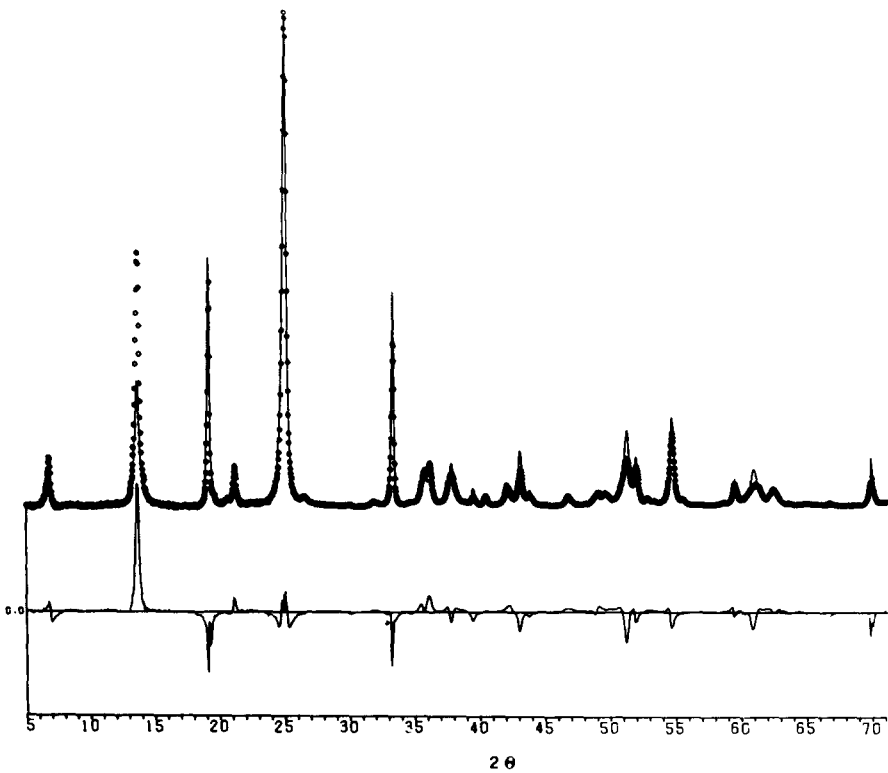


FIG. 3. Experimental (O), calculated (—), and difference (lower) profiles for $\text{Zr}(\text{HPO}_4)_{0.85}(\text{HPO}_3)_{1.15} \cdot 0.5\text{H}_2\text{O}$.

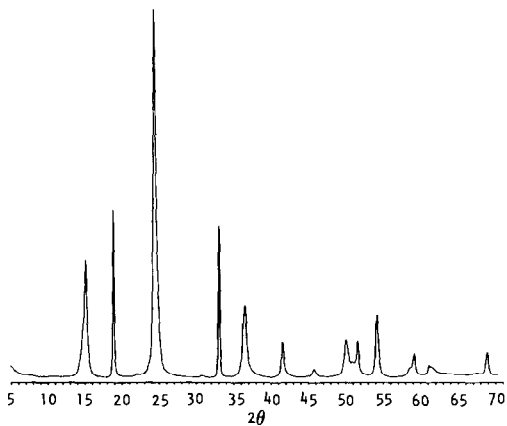


FIG. 4. X-Ray powder pattern of $\text{Zr}(\text{HPO}_4)_{0.36}(\text{HPO}_3)_{1.64}$.

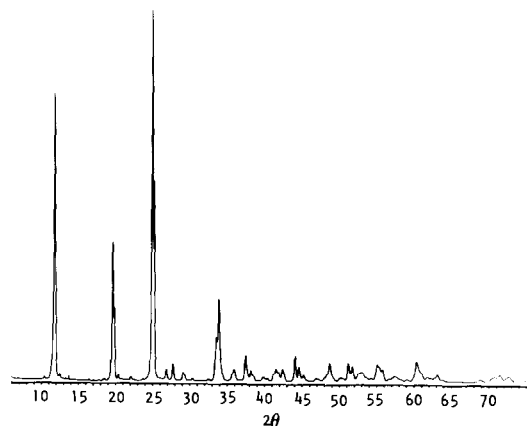


FIG. 5. X-Ray powder pattern of $\text{Zr}(\text{HPO}_4)_{1.46}(\text{HPO}_3)_{0.54} \cdot \text{H}_2\text{O}$.

In the case of zirconium phosphate-phosphite with low phosphate content (ZPP-1), the distribution remains asymmetric, one side of the sheet containing phosphites only. Because of the high concentration of phosphites on both sides of the sheets, the stacking remains essentially that of the pure α -zirconium phosphite; however, owing to the sheet asymmetry, the structural periodicity includes in this case two layers (see Table I). The experimental X-ray patterns of ZPP-1 is reported in Fig. 4.

Finally, in ZPP-3 there is a random distribution of phosphate and phosphite groups on both sides of each sheet. Owing to the excess of phosphates on both sides of the sheets, the resultant structure is practically identical to that of the α -zirconium phosphate with a slight dependence of the interlayer distance on the amount of phosphite replacing the phosphate groups (Table I).

The X-ray pattern of ZPP-3 is reported in Fig. 5. Structure refinements of the various ZPP phases, as well as of the derived ones obtained by ion-exchange or intercalation procedures, are now being undertaken.

We are also carrying out a systematic structural investigation of numerous other α -Zr(RPO_3)_x($R'PO_3$)_{2-x} layered compounds in order to collect some general information how the length, size and chemical nature of the R and R' groups affect their asymmetric distribution on the opposite sides of the sheets and the stacking sequence of the layers.

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